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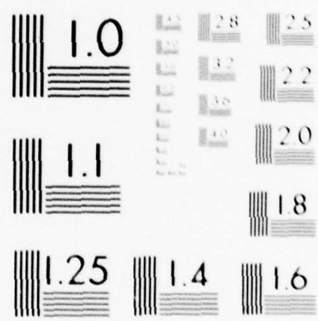

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TEMPERATURE PROFILE IN Li/SO_2 CELLS DURING DISCHARGE

BY S. DALLEK R. F. BIS F. M. BOWERS

RESEARCH AND TECHNOLOGY DEPARTMENT

15 DECEMBER 1978

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Li/SO_2 cells have been discharged at various rates to study the distribution of heat within the cells and to determine the conditions under which Li/SO_2 batteries may be safely used by the Navy.

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SUMMARY

The Li/SO_2 electrochemical system is presently employed as the power source in many Navy devices. However, several safety incidents have occurred with this system in which cells have vented toxic fumes, exploded, and caught fire. This initial, limited investigation was undertaken to study the heat distribution within these cells during discharge as part of an overall program to determine conditions under which Li/SO_2 cells may be safely used by the Navy.

J. R. Dixon

J. R. DIXON
By direction

PREFACE

The authors wish to thank D. Warburton for helpful discussions during the course of this work, D. Ernst for originally suggesting the thermocouple positioning, L. Leach and J. Gott for devising and constructing the electronic circuitry and data acquisition equipment, and T. Peacock for providing computer analysis of the data.

CONTENTS

	Page
INTRODUCTION	5
EXPERIMENTAL	5
RESULTS AND DISCUSSION	6
CONCLUSIONS	7

ILLUSTRATIONS

Figure		Page
1	Thermocouple Arrangement within Cell	9
2	Test Circuit for Cell Discharges	10
3	Discharge of Thermally Insulated Li/SO_2 D-Cells at 1 Amp Rate to 2 V Cutoff	11
4	Discharge of Thermally Insulated Li/SO_2 D-Cells at 2 Amp Rate to 2 V Cutoff	12
5	Discharge of Thermally Insulated Li/SO_2 D-Cells at 4 Amp Rate to 2 V Cutoff	13
6	Discharge of Thermally Insulated Li/SO_2 D-Cells at 8 Amp Rate to 2 V Cutoff	14
7	Discharge of Thermally Insulated Li/SO_2 D-Cells at 10 Amp Rate to Venting	15
8	Discharge of Thermally Insulated Li/SO_2 D-Cells at 6 Amp Rate to Venting	16
9	Discharge of Thermally Insulated Li/SO_2 D-Cells at 4 Amp Rate to Venting	17
10	Discharge of Thermally Insulated Li/SO_2 D-Cells at 3 Amp Rate to Venting	18
11	Plot of Cell Capacity vs. Discharge Rate to 2 V Cutoff	19
12	X-ray of Cell Before and After Discharge	20

TABLES

Table		Page
1	Summary of Discharge Results	21

INTRODUCTION

The Li/SO_2 electrochemical system is one of the highest energy density systems developed during the last decade and is presently employed as the power source for several Navy applications. However, safety considerations have raised the questions of the optimum conditions and operational limits under which this system can be of maximum use to the Navy.[1-5] The present work was undertaken to study the heat distribution within these cells during various rates of discharge to determine conditions under which Li/SO_2 batteries may be safely used by the Navy.

EXPERIMENTAL

Instrumented D-size spirally-wound 3 volt 10 Ah cells (Mallory) were used. Cells were stored at ambient temperature for about 1 year and all had an open-circuit potential of 2.99 ± 0.01 V. The cells were instrumented with four iron-constantan thermocouples to determine the heat distribution within the cell during discharge. The arrangement of the thermocouples is shown in Figure 1. One thermocouple (A) was positioned inside the cell between the positive terminal and the cathode current collector; the second (B) was positioned midway between the center post and the can and also midway between the top and bottom of the cell; the third (C) was positioned outside the can immediately adjacent to the connection of the lithium anode to the can; and the fourth (D) was a control thermocouple in contact with the can and positioned 180° from the third thermocouple. This arrangement

1. D. L. Warburton, "Safety, Shelf Life and Low Rate Discharge Characteristics of Organic Solvent Lithium Batteries", Proc. 26th Power Sources Symposium, p.34 (May 1974).

2. E. S. Brooks, "Evaluation of Designs for Safe Operation of Lithium Batteries", ibid., p.42.

3. H. Taylor and B. McDonald, "Abuse Testing of Li/SO_2 Cells and Batteries", Proc. 27th Power Sources Symposium, p.66 (June 1976).

4. G. DiMasi, "Behavior of Li/SO_2 Cells Under Forced Discharge", ibid., p.75.

5. F. M. Bowers, "Safe, Useful Lithium Batteries For The Navy", NSWC/WOL/TR 77-140, 15 December 1977.

of thermocouples was chosen to provide useful information to determine the possible causes of heat build-up within these cells and the resulting safety problems which can occur. A diagram of the constant current test circuit used is shown in Figure 2.

Data were recorded using a conventional data acquisition system; in addition, the occurrence of venting was determined, using a strip chart recorder, from the output of two thermocouples positioned immediately above the vents on the end of the battery.

The experimental procedure consisted of discharging the batteries in pairs at a low rate (1 A), to a cutoff voltage of about 2 V, progressing to higher rates until venting occurred. If either test cell vented at a particular rate, the run would be repeated with a new cell at a lower rate. Furthermore, discharges were repeated at the lower rates, at which cells did not vent when the discharge was terminated at 2 V, to determine if venting would occur at lower voltages. Test cells were thermally insulated with Fiberfrax insulation to simulate the heat generation during discharge within a battery containing several cells. The cells were positioned behind a shield inside a hood to eliminate possible hazards from explosions or venting of noxious fumes during discharge.

Cells were also X-rayed before and after discharge to determine what structural changes, if any, occurred during discharge.

RESULTS AND DISCUSSION

Typical results are shown in Figures 3-7 wherein temperature vs. time is plotted for the four thermocouples (A-D), and cell voltage vs. time is plotted for each cell for discharges down to a cutoff of about 2 V. At the 1 A, 2 A, and 4 A rates, no venting occurred to the 2 V cutoff. However, at the 8 A rate, both cells vented quietly with a slight hissing sound, one at 2.2 V and the other at 1.8 V. A final high-rate discharge was run at the 10 A rate. At this rate, both cells vented quietly at first but shortly thereafter (within a few minutes) vented violently with a loud whooshing sound and caught fire. Flames and smoke were expelled from the end of the battery on which the vents were constructed (the batteries were horizontally positioned during discharge), and the plastic battery coating and plastic covering on the connecting wires ignited. During the quiet venting, both cells went into voltage reversal (-6 V and -9 V) and were thus being driven in reverse prior to venting violently. It is of particular interest to note that, at the 10 A rate, at least one of the thermocouples in each cell reached a temperature of about 188°C, which is above the melting point of lithium (180.5°C).

Figures 8-10 show the curves for discharges which were repeated at some of the lower rates (< 8 A) and which were allowed to proceed past the 2 V cutoff point until venting occurred or until the cell went into voltage reversal. At the 6 A rate, one cell vented when its voltage dropped below 1 V to about +0.8 V, while the other cell vented when it went into voltage reversal (-0.8 V). At the 4 A rate, both cells dropped to approximately the same voltage prior to venting; one cell vented after reaching a voltage of +0.53 V while the other cell vented after its voltage had reached +0.47 V (the voltage in this second case was erratic just prior to venting, occasionally becoming negative). At the

3 A rate, the voltage of both cells again stabilized at about this same value (+0.45 V). Both cells then went into voltage reversal prior to venting, the voltage of one cell reaching -5.5 V and the other cell -18 V. This second cell vented violently with the generation of smoke and with ensuing fire. The resulting temperature in the region of the cell around thermocouple B was greater than the detection limit of the thermocouple (>870° C). Secondary fires were also generated as in the case of the cells discharged at the 10 A rate.

As shown by these curves, the highest temperature during discharge was usually recorded by thermocouple B (center of cell) although occasionally thermocouple A would detect a slightly higher temperature. In only one case, at the highest rate (10 A) tested, was there any evidence of the temperature vs. time curves being out of phase. The term "phasing" in this case means that the times of peak temperatures of each of the four thermocouples were compared. If they occurred at the same time the thermocouples were said to be in phase. If they occurred at different times the thermocouples were said to be "out of phase". It should be noted that the observation that the temperature vs. time curves were always in phase at discharge rates below 10 A may be due to the inability of our data acquisition system to sample at a rate faster than one channel every fifteen seconds. This type of comparison of the temperature peaks with time was made to determine possible areas of heat generation within the cell.

A summary of the discharge results is presented in Table I. A plot of cell capacity vs. discharge rate is presented in Figure 11.

X-rays taken of cells before and after discharge showed little structural difference except in those cases where the internal temperature of the cell increased drastically during discharge. Typical X-ray results of a cell which vented violently are shown in Figure 12. The cell is viewed down its center from above before and after discharge in a and b, respectively, and is viewed from the side before and after discharge in c and d, respectively. The cell vented violently and caught fire after being discharged at the 3 A rate down to +0.45 V and then into reversal. Views b and d show substantial internal cell destruction from the melting of the lithium anode and the polypropylene separator.

CONCLUSIONS

The temperature profiles obtained during discharge of instrumented Li/SO_2 cells show that the greatest temperature is generally achieved in the region around thermocouple B which is positioned midway between the center post and the can and also midway between the top and bottom of the cell. Occasionally, a slightly higher temperature is reached at thermocouple A which is positioned inside the cell between the positive terminal and the cathode current collector. Thus, during a discharge of a thermally insulated cell, the greatest amount of heat builds up in the center of the cell. The small temperature gradients recorded between thermocouples, the nearly linear temperature increases, and the fact that the temperature vs. time curves were found to be in phase suggest that, except for the highest rate tested (10 A), the heat buildup within these cells was purely resistive in nature.

Concerning the safe use of these cells, it has been demonstrated that at very high rates of discharge, e.g. 10 A, cells may vent violently and cause a fire.** At this high rate of discharge, the internal cell temperature exceeded the melting point of the lithium anode which is in the form of an unsupported strip. The polypropylene separator would also be molten at this temperature. Thus, contact of the highly reactive molten lithium with other reactive species in the cell is possible under these conditions and could result in a very exothermic chemical reaction. At the lower rates, e.g. 3 A, explosive venting and fires may still occur if an inferior cell in a series stack is driven into voltage reversal. In one study[4], Li/SO_2 cells have exploded and burned when discharged at the 1 A rate. In another study[2], an explosion and fire occurred within 45 seconds when the battery was reverse discharged at the 2 A rate.

In summary, this limited investigation has shown that venting of Li/SO_2 cells, which may sometimes be quite violent and accompanied by fire, is a function both of discharge rate and depth of discharge. Thus, cells may vent violently during high rate discharge or, even during low rate discharge, if the discharge continues at low cell voltage (+0.45 V); the hazard is especially great if an inferior cell in a series stack is driven into voltage reversal.

Since high pressure buildups within the cell may be caused not only by resistive heating but also by parasitic exothermic chemical reactions,[4] a recent study of mixtures of various Li/SO_2 cell components and/or postulated discharge products was conducted to identify possible explosion-causing chemical combinations.[6] Future work is planned to identify the products formed during discharge of Li/SO_2 cells under various conditions including those of forced discharge.

** In a similar study[3], thermally insulated D-size Mallory Li/SO_2 cells were driven into voltage reversal for extended periods with no explosion hazards (only quiet venting) reported even at a discharge rate of 10 A/cell.

6. W. P. Kilroy and S. Dallek, "Differential Scanning Calorimetry Studies of Possible Explosion-Causing Mixtures in Li/SO_2 Cells", J. Power Sources 3(3), 291 (1978). See also NSWC/WOL/TR 78-156, 13 Nov 1978.

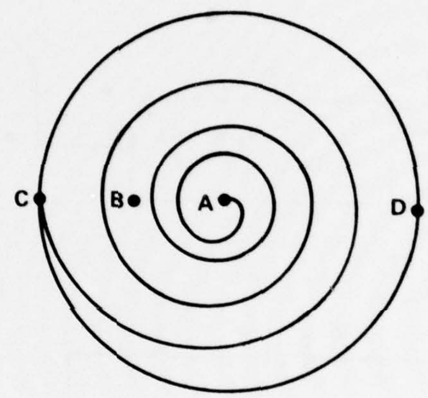


FIGURE 1 ARRANGEMENT OF THERMOCOUPLES IN CELL (VIEWED FROM TOP OF CELL)

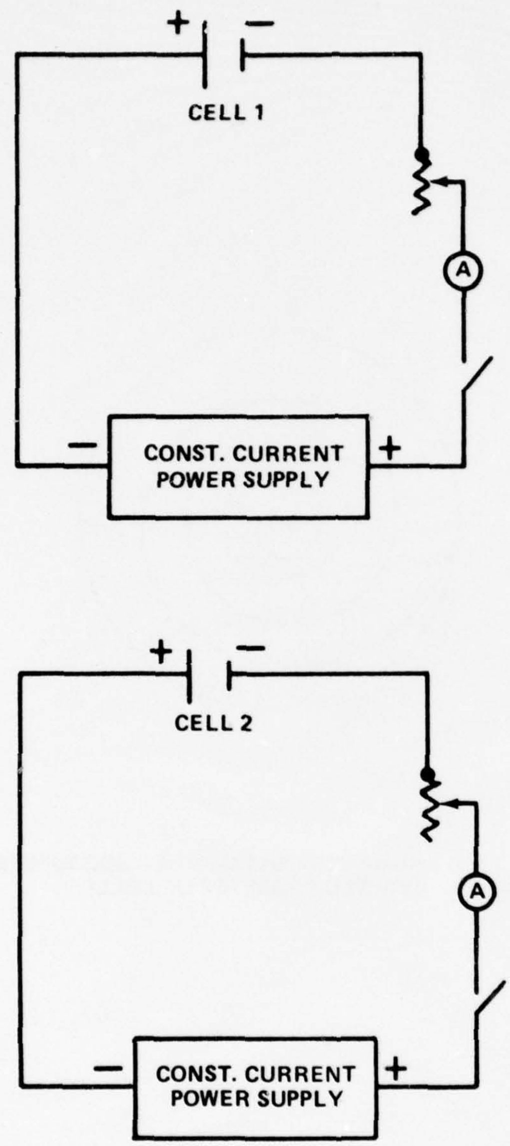


FIGURE 2 TEST CIRCUIT FOR CELL DISCHARGES

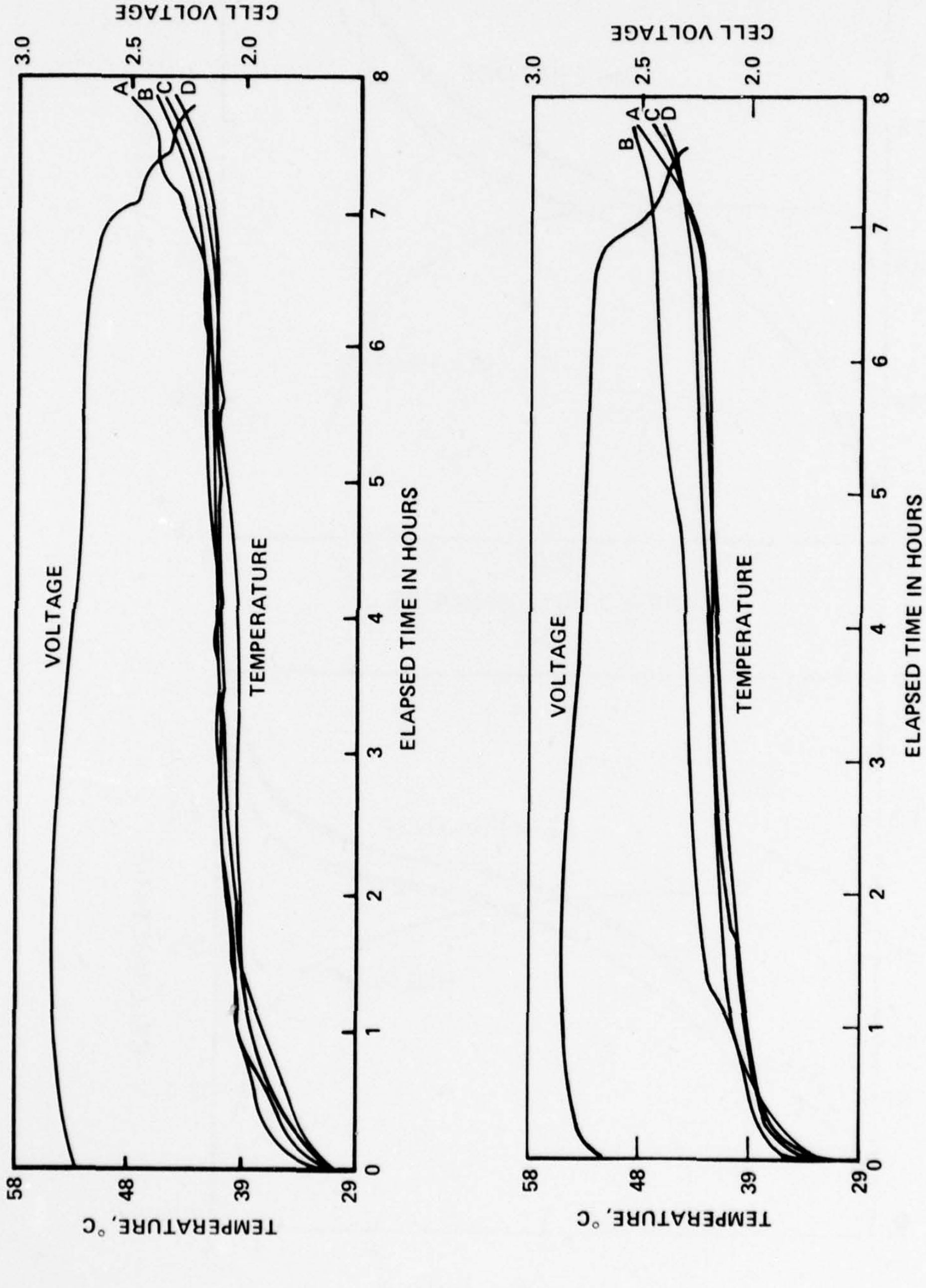


FIGURE 3. DISCHARGE OF THERMALLY INSULATED Li/SO_2 D-CELLS AT 1 AMP RATE TO 2V CUTOFF.

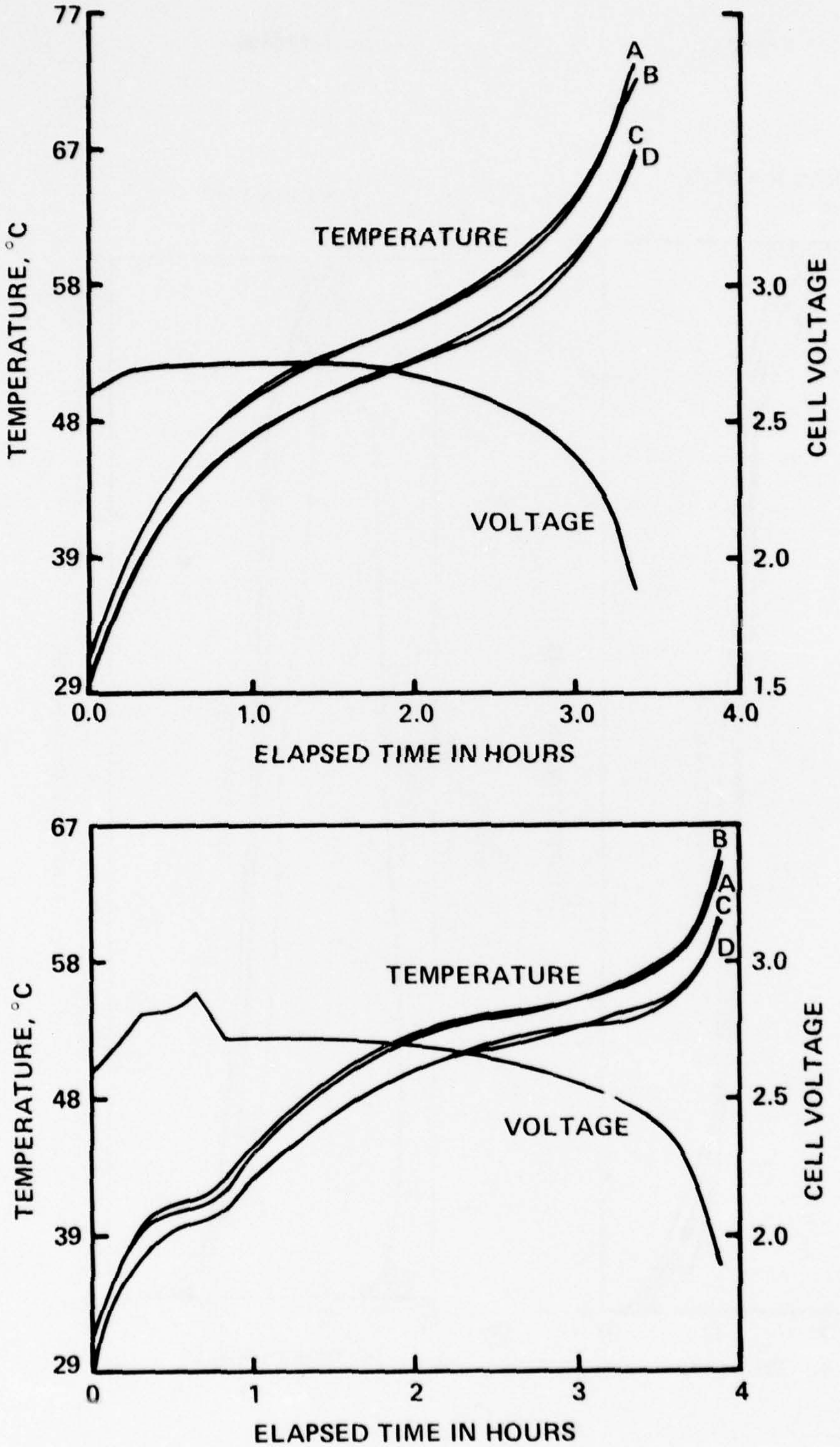
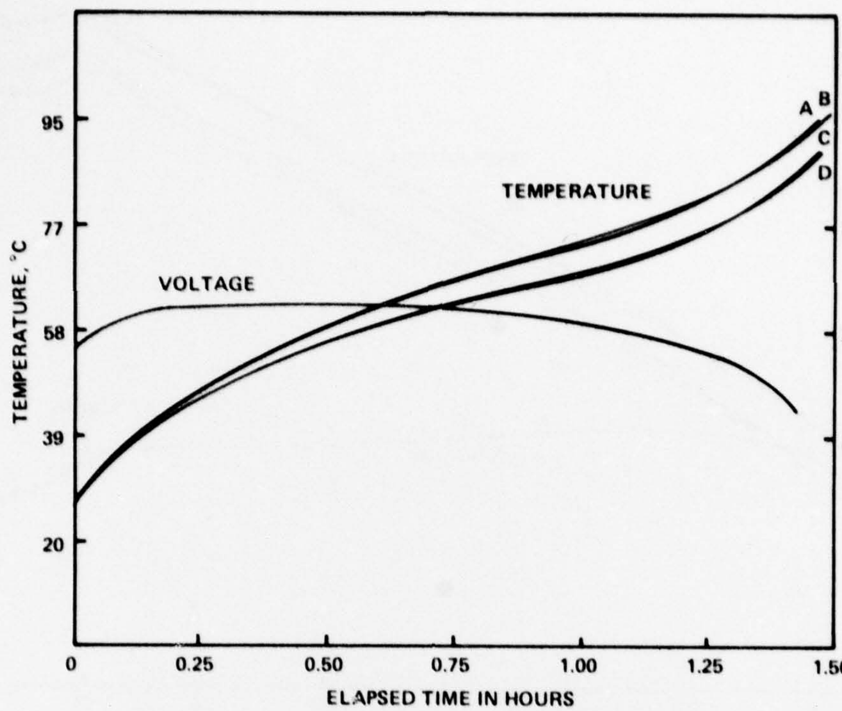


FIGURE 4. DISCHARGE OF THERMALLY INSULATED Li/SO_2 D-CELLS AT 2 AMP RATE TO 2V CUTOFF.



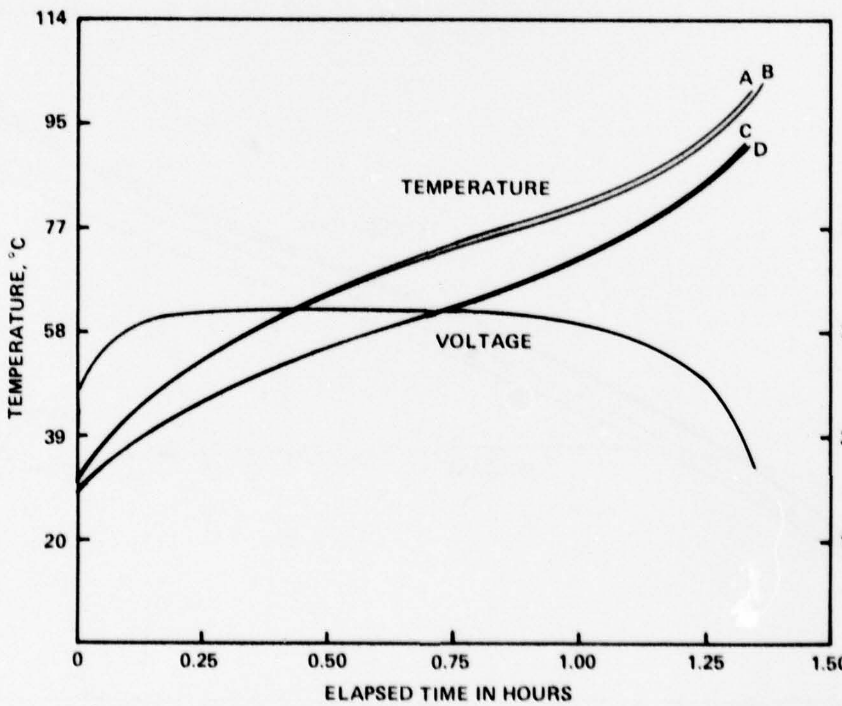


FIGURE 5. DISCHARGE OF THERMALLY INSULATED Li/SO_2 D-CELLS AT 4 AMP RATE TO 2V CUTOFF.

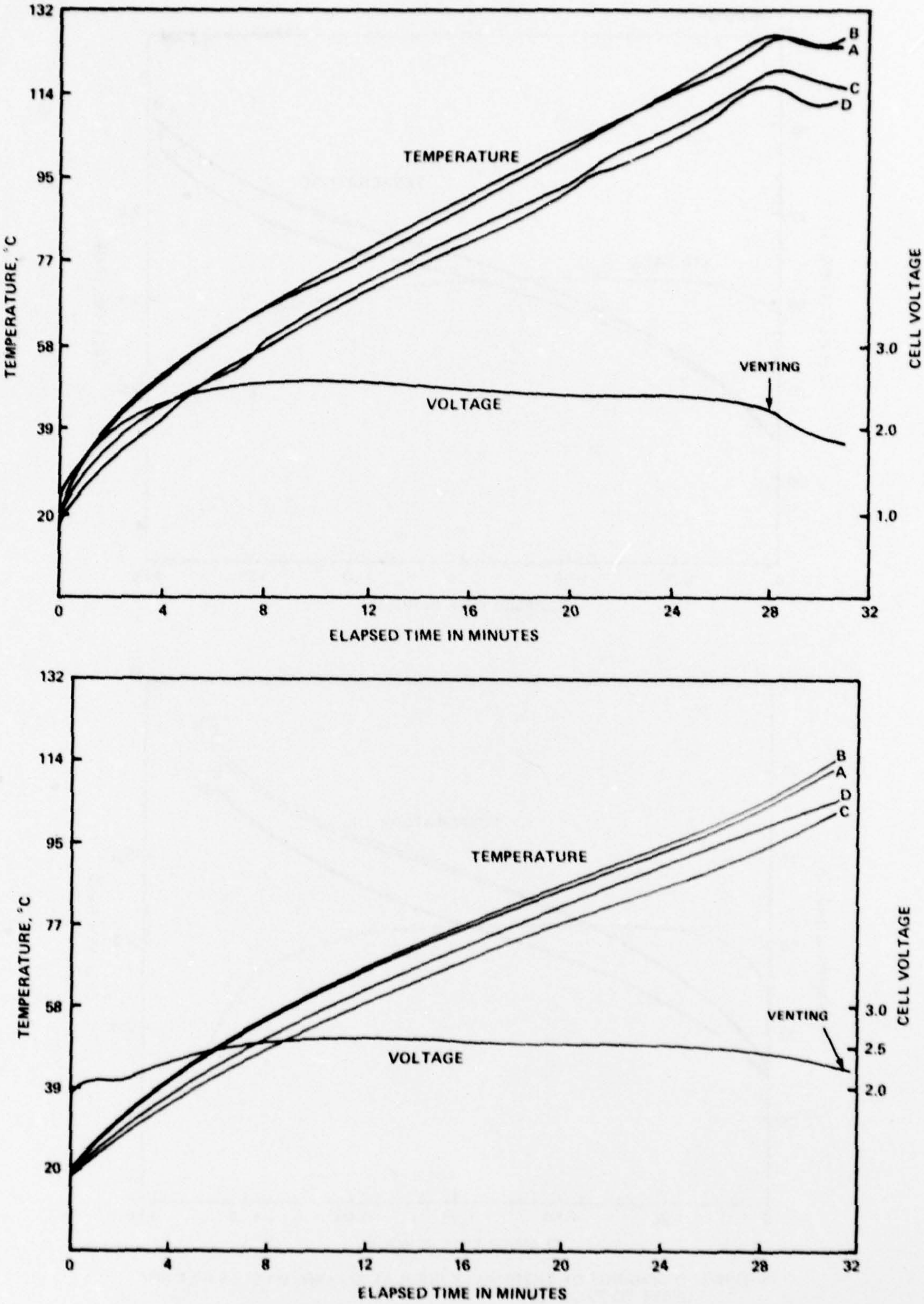


FIGURE 6. DISCHARGE OF THERMALLY INSULATED Li/SO_2 D-CELLS AT 8 AMP RATE TO 2V CUTOFF.

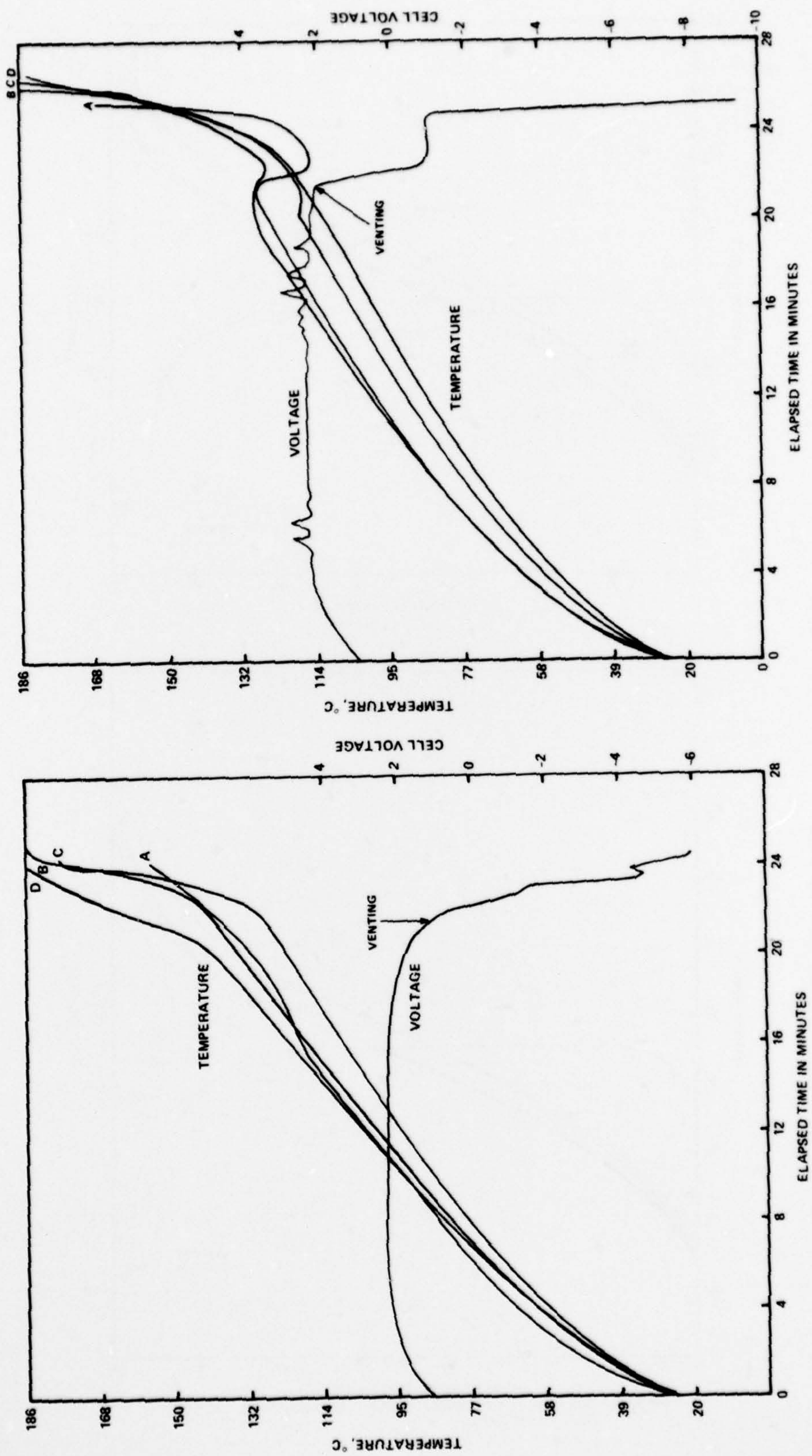
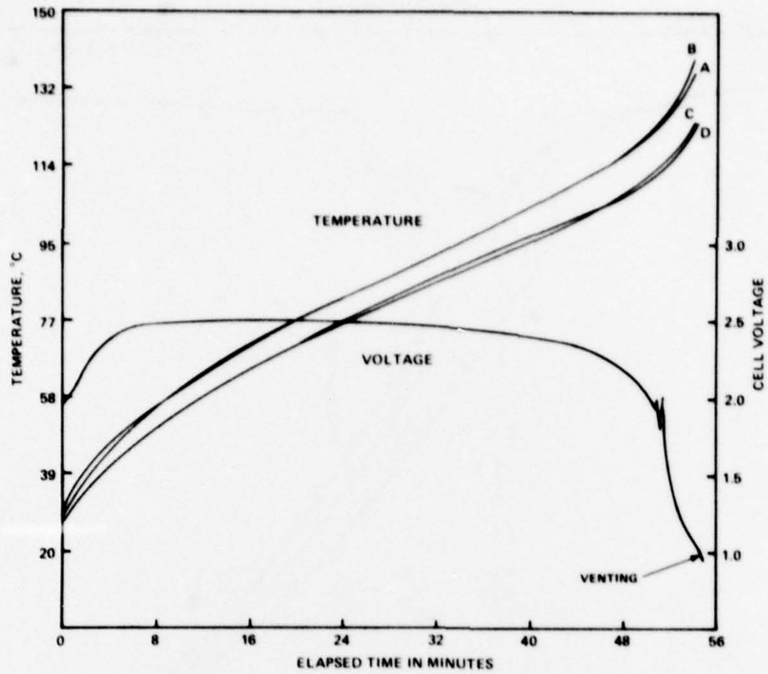


FIGURE 7. DISCHARGE OF THERMALLY INSULATED Li/SO_2 D-CELLS AT 10 AMP RATE TO VENTING.



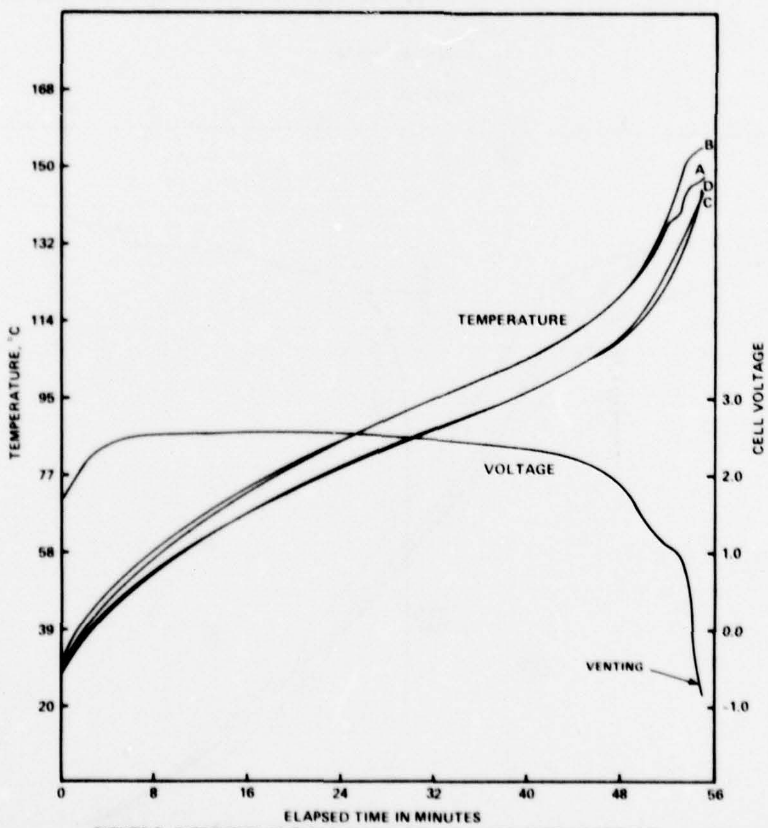
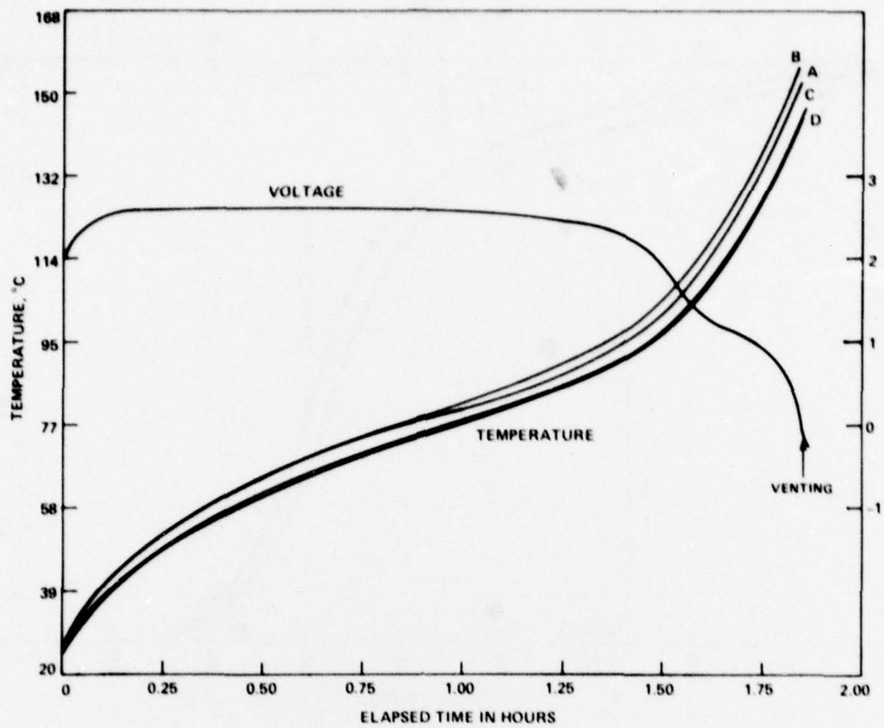


FIGURE 8. DISCAHRGE OF THERMALLY INSULATED Li/SO_2 D CELLS AT 6 AMP RATE TO VENTING.



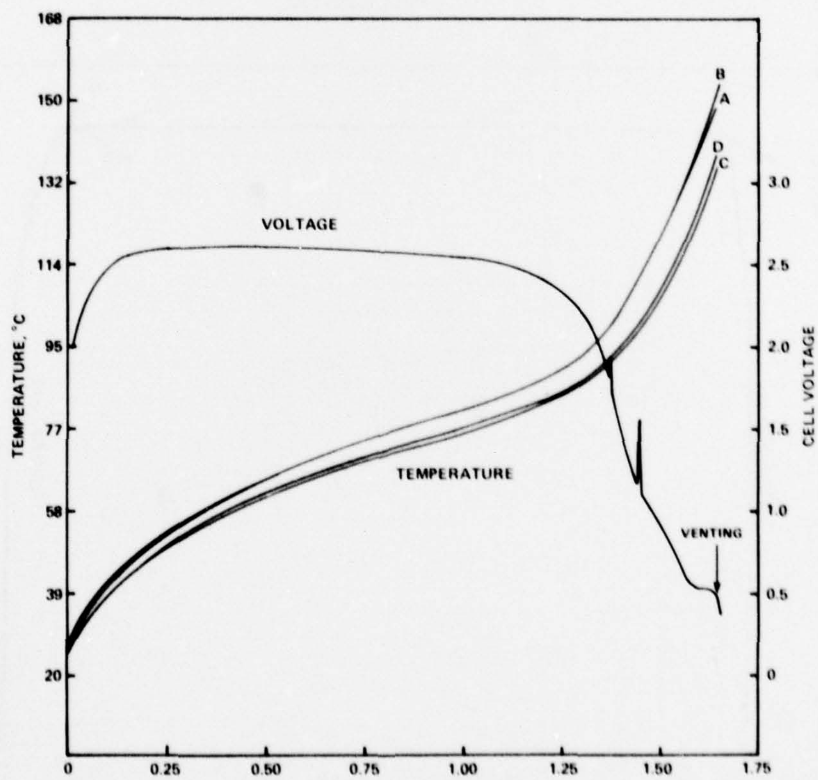
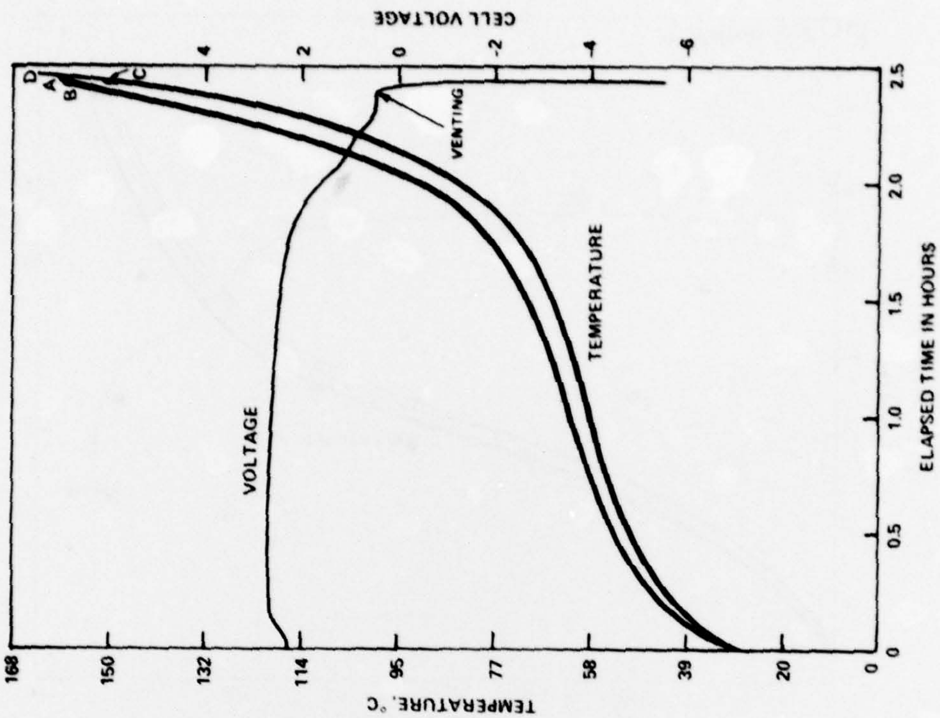


FIGURE 9. DISCHARGE OF THERMALLY INSULATED Li/SO_2 D-CELLS AT 4 AMP RATE TO VENTING.



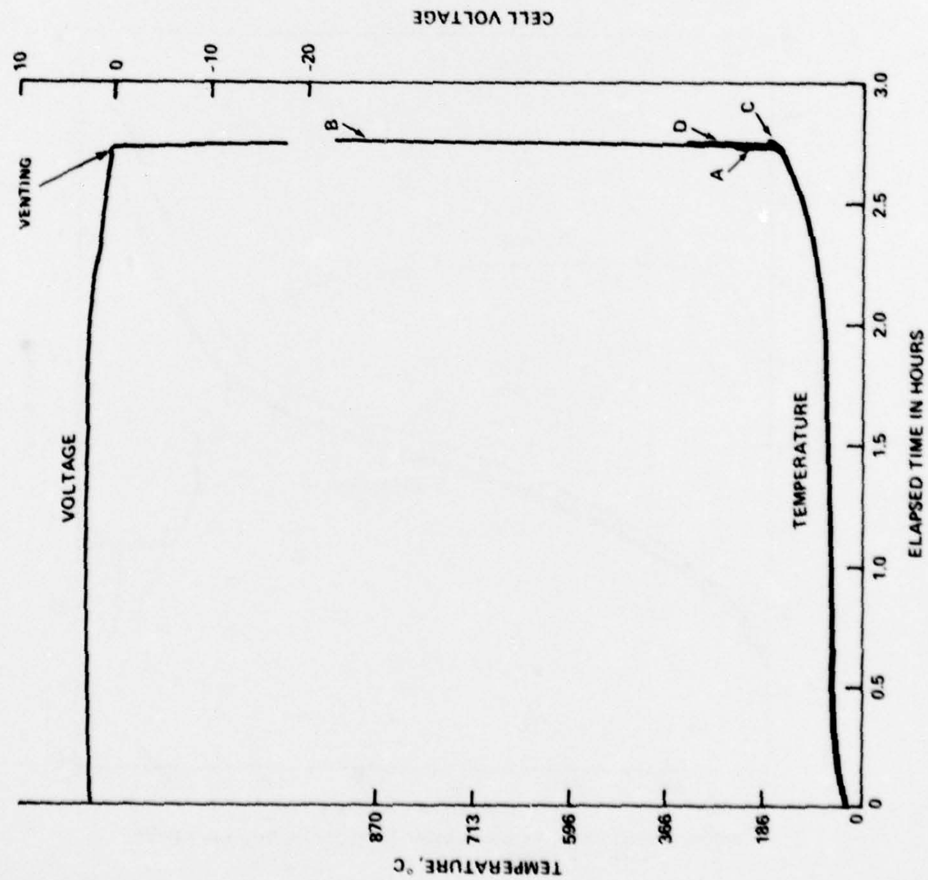


FIGURE 10. DISCHARGE OF THERMALLY INSULATED Li/SO_2 D-CELLS AT 3 AMP RATE TO VENTING.

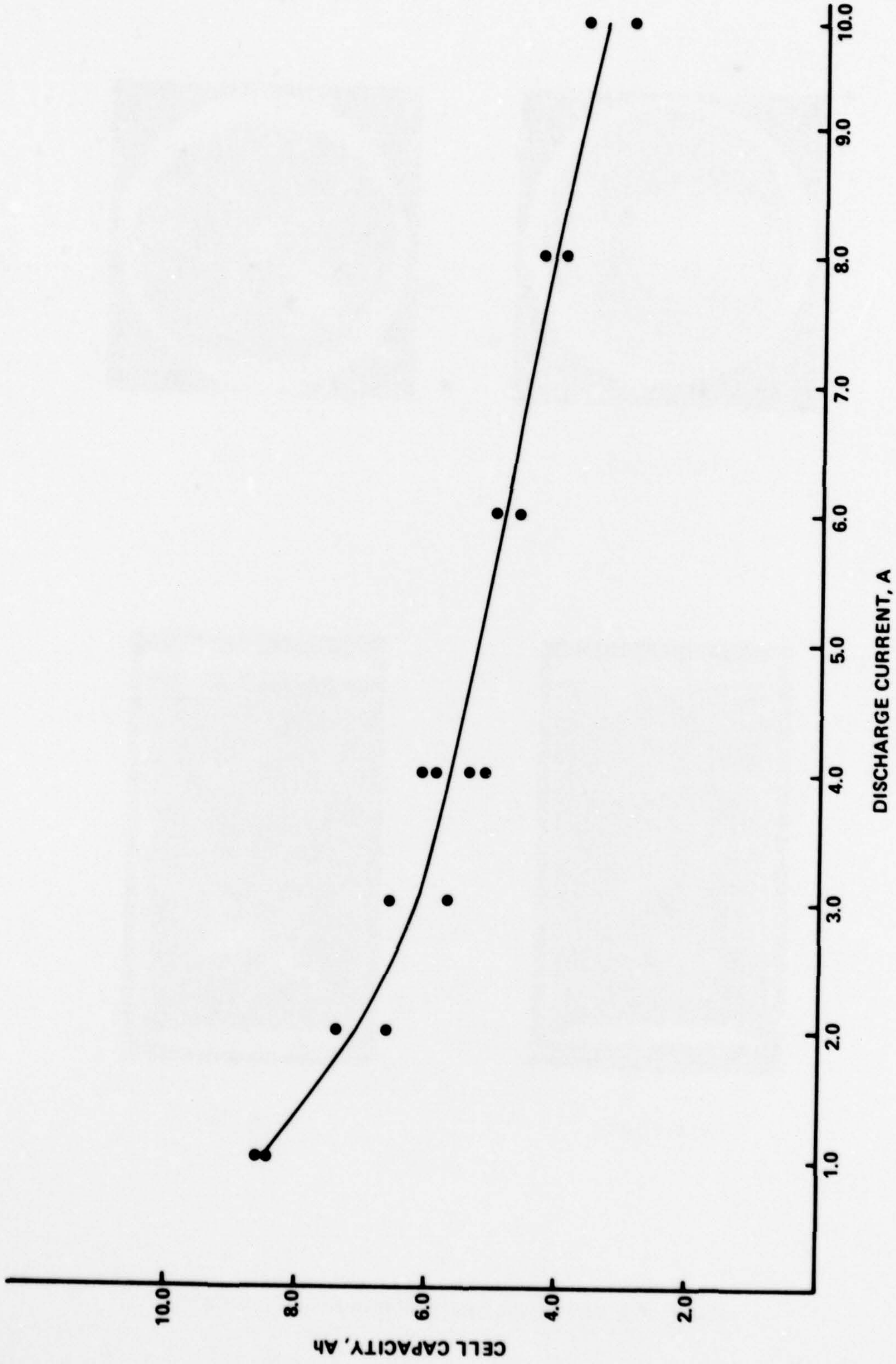
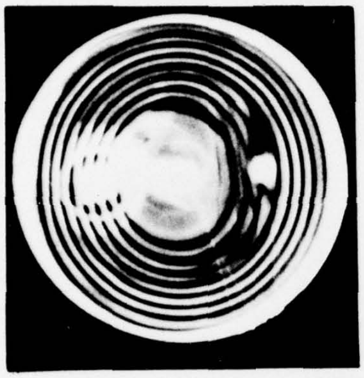


FIGURE 11 CELL CAPACITY VS. DISCHARGE RATE TO 2 VOLT CUT-OFF



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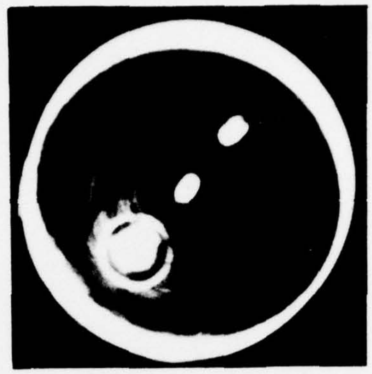

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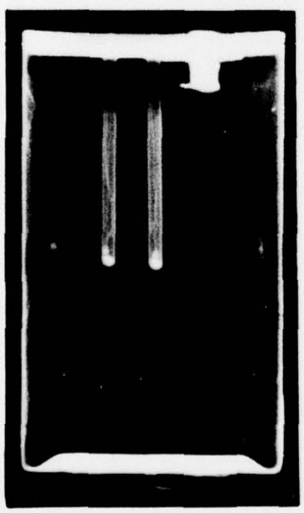

(C) BEFORE

(D) AFTER

FIGURE 12 X-RAY OF CELL BEFORE AND AFTER DISCHARGE

Table I. Summary of Discharge Results

Discharge Current (A)	Current Density* (mA/cm^2)	A-h (to 2 V)	Venting (to 2 V)	Venting (< 2 V)	Violent Venting + Fire
1	2.1	8.5			
1	2.1	8.5			
2	4.2	6.6			
2	4.2	7.4			
3	6.4	5.7		✓	
3	6.4	6.6		✓	✓
4	8.5	5.2			
4	8.5	6.0			
4	8.5	6.0		✓	
4	8.5	5.4		✓	
6	12.7	4.7		✓	
6	12.7	5.0		✓	
8	17.0	4.0	✓		
8	17.0	4.3	✓		
10	21.2	3.0	✓		✓
10	21.2	3.7	✓		✓

*Based on an anode area of 471.8 cm^2

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